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(21) International Application Number: PCT/AU94/00550 (22) International Filing Date: 13 September 1994 (13.09.94) (30) Priority Data: PM 1177 13 September 1993 (13.09.93) AU (71) Applicants (for all designated States except US): THE AUSTRALIAN NATIONAL UNIVERSITY [AU/AU]; Acton, ACT 2601 (AU). WESTRALIAN SANDS LIMITED [AU/AU]; Jenkin Road, Capel, W.A. 6271 (AU). (72) Inventors; and (75) Inventors/Applicants (for US only): CALKA, Andrzej [PL/AU]; 178 Majura Avenue, Ainslie, ACT 2602 (AU). MILLET, Patrice [FR/AU]; 94 Gilmore Crescent, Garran, ACT 2605 (AU). NINHAM, Barry, William [AU/AU]; 18 Booth Crescent, Cook, ACT 2614 (AU). WILLIAMS, James, Stanislaus [AU/AU]; 15 Twynam Street, Holder, ACT 2611 (AU). (74) Agents: DUNCAN, Alan, David et al.; Davies Collison Cave, 1 Little Collins Street, Melbourne, VIC 3000 (AU).		(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD). Published <i>With international search report.</i>
(54) Title: ILMENITE PROCESSING USING COLD MILLING		
(57) Abstract <p>High energy ball milling of particulate ilmenite (or other titaniferous ore) at room temperature, for periods of up to 300 hours, in the presence of a suitable additive, produces a nanostructural powder from which at least a major proportion of the iron in the titaniferous ore can be leached. The additive may be a reducing agent (for example, amorphous boron), a long chained hydrocarbon (for example, dodecane) or a surfactant (preferably dihexadecyl dimethyl ammonium acetate, or didodecyl dimethyl ammonium bromide, or didodecyl dimethyl ammonium acetate, or didodecyl dimethyl ammonium hydroxide, or sodium didodecyl sulphate). The leaching is preferably effected using 4M hydrochloric acid at a temperature of from 80 °C to 100 °C.</p>		

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TITLE: "ILMENITE PROCESSING USING COLD MILLING"

Technical Field

This invention concerns the treatment of minerals containing titanium dioxide and iron, which are generally called titaniferous minerals. The most common of these minerals is ilmenite. More particularly, this invention concerns cold milling of particulate titaniferous minerals to form nanostructured products from which the iron content (or a significant amount of the iron content) of the mineral can be removed by a leaching process.

Background to the Invention

Ilmenite, FeTiO_3 , and titaniferous minerals generally, are relatively inert minerals that have long been a major source of titanium dioxide, TiO_2 , which is used as a white pigment in paints, to produce welding rods, and in the cosmetic and ceramics industries. Extraction of the iron from the ilmenite and other titaniferous minerals has been, and still is, an expensive undertaking.

Most of the currently used metallurgical processing of ilmenite includes hot acid leaching of the particulate mineral, with associated environmental problems. For example, the "sulphate route" for the extraction of titanium dioxide from ilmenite involves the steps of

- (a) mixing dry milled ilmenite with 85 to 92 per cent sulphuric acid;
- (b) heating the mixture of ground ilmenite and sulphuric acid to a temperature of about 160°C , at which temperature an exothermic reaction is initiated, the

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product of this reaction being a mixture of ferrous, ferric and titanium sulphates;

- (c) forming an aqueous (or weakly acid) solution of the mixture of sulphates, then reducing the ferric sulphate to ferrous sulphate with scrap iron;
 - (d) clarifying the solution by sedimentation;
 - (e) removing the iron in the solution by crystallisation (as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$); and
 - (f) extracting the titanium dioxide using hydrolysis.
- 10 Another technique that is used to process ilmenite is the so-called "chloride route", which involves the chlorination of impure rutile using gaseous chlorine at a temperature in the range of from 650°C to $1,150^\circ\text{C}$ to form titanium tetrachloride (TiCl_4). The TiCl_4 is then oxidised to
- 15 produce pure titanium dioxide.

The "Becher" process is also used to upgrade ilmenite - to remove iron and provide a feedstock for the "chloride route". In the Becher process, ilmenite is reacted with coal and sulphur in an iron reduction kiln at 1100°C . This

20 reaction reduces the iron in the ilmenite to the metallic form. After cooling the products of the reaction, the iron is rusted out in slurry form with ammonium chloride acting as a catalyst for the rusting. The remaining iron compounds are removed by leaching with sulphuric acid.

25 One of the more promising alternative ilmenite processing methods, developed jointly by Commonwealth Scientific and Industrial Research Organisation and Murphys Pty Limited, known as the "Murso process", is described in the

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specification of Australian patent No 416,143. The Murso process uses an oxidation of the ilmenite to convert substantially all the iron to the ferric state, then reduction of the oxidised material to convert substantially all the ferric iron to the ferrous state. These steps, of oxidation of the ilmenite followed by its reduction, produce a material which has an enhanced reactivity, from which the iron can be leached with dilute hydrochloric acid. The cost of using hydrogen as the reducing agent and the cost of regeneration of the hydrochloric acid used for leaching have made the adoption of the Murso process commercially unattractive. Several attempts have been made to modify the Murso process to improve its economics, but at the time of writing this specification, it has not been adopted commercially.

The search for other improved methods of producing rutile from ilmenite has continued.

Disclosure of the Present Invention

The prime object of the present invention is to provide a method of treating ilmenite and other titaniferous minerals to convert such minerals into a form from which the iron content can be removed by a simple leaching process.

This objective is achieved by a cold milling process.

Ball milling of ores, with and without additives to facilitate the comminution process (the reduction of particle size) is not new. The early potential of ball milling for the reduction and extraction of ores, however,

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has generally not been fulfilled, and interest in such ore processing technology has waned. The development of a new form of high energy ball mill at The Australian National University, and the success that has been achieved in
5 mechanical alloying work with that ball mill (see, for example, the specifications of International Patent Applications Nos PCT/AU91/00248, PCT/AU92/00073 and PCT/AU94/00057), have stimulated new interest in the cold milling of ores. That new ball mill, which is described in
10 the specification of International patent application No PCT/AU90/00471 (WIPO Publication No WO 91/04810), enables controlled-energy milling of a charge to be effected. The present inventors have now discovered that under certain milling conditions, ilmenite can be reduced
15 while being converted into a nanostructural form, and that iron can be removed from this product (for example, using hydrochloric acid at a temperature of about 100°C).

The basic requirements of the cold milling process are:
(i) that high energy milling is carried out at room
20 temperature for a sufficient time period (up to 300 hours) to produce a powder having a nanostructural form, and
(ii) that the milling is effected in the presence of suitable additives to the ball mill charge.

Thus, according to the present invention, there is provided
25 a method of treatment of a titaniferous ore to facilitate the removal of iron from the ore to produce rutile, the method comprising high energy milling of the ore in particulate form in the presence of a suitable additive for a period sufficient to form a nanostructural titaniferous
30 product.

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The additives include both solid and liquid reducing agents. Amorphous boron has been found to be a useful additive, as have a range of surfactants and organic materials (particularly long chained hydrocarbons). Among
5 the surfactants which may constitute the additive of the present invention are:

- (a) dihexadecyl dimethyl ammonium acetate (DHDAAC);
- (b) didodecyl dimethyl ammonium bromide (DDAB);
- (c) didodecyl dimethyl ammonium acetate (DDAA);
- 10 (d) didodecyl dimethyl ammonium hydroxide (DDAOH); and
- (e) sodium didodecyl sulphate (SDDS) - an anionic double chained surfactant.

Dodecane is a preferred long chained hydrocarbon which can be used as the additive of this invention.

- 15 To extend this method to include the production of rutile, the milled ore must subsequently be leached to extract the iron from it (for example, using hydrochloric acid at a temperature of about 100°C).

Preferably the milling is carried out in a ball mill of the
20 type described and claimed in the specification of International patent application No PCT/AU90/00471.

A better understanding of the present invention will be obtained from the following description and discussion of experimental work in connection with the cold milling of
25 ilmenite, which has been undertaken by the present inventors.

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Description of Cold Milling Work

The present inventors hypothesised that subjecting a particulate titaniferous material to prolonged milling should change the mineral into a reactive nanostructural form, from which it should be possible to remove α -Fe by acid leaching or by magnetic separation. When this hypothesis was tested, simple milling of ilmenite did not produce a reactive nanostructural form of the mineral. However, milling ilmenite with an additive to the ball mill charge, surprisingly, did yield a reactive nanostructural product.

A series of experiments were then performed with ilmenite (in its mineral sand form) to investigate this phenomenon further. In each experiment, the particulate ilmenite was subjected to prolonged high-energy milling in a ball mill of the type described in the specification of International patent application No PCT/AU90/00471. (It will be appreciated that milling in other types of high energy ball mill for an appropriate period of time should have the same effect.) The milling was effected for a period sufficient to convert the particulate ilmenite charge of the ball mill into a nanostructural material. This required high energy ball milling for a period of time which depended upon the milling conditions and the additive(s) to the ball mill charge.

The milled samples were then leached with no further treatment.

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At different stages of the experiments, the composition of each sample was assessed using one or more of the following techniques: x-ray diffraction; Mossbauer spectroscopy; transmission and scanning electron microscopy; atomic
5 absorption spectrometry; Rutherford backscattering spectrometry. In particular, structural development of the as-milled samples was monitored by x-ray diffraction of cobalt K α radiation using a Phillips diffractometer, and Rutherford backscattering spectrometry was used to analyse
10 the presence of iron in chemically leached samples.

A range of additives were used with the initial charge of the ball mill. In each experiment, the additive remained in the charge of the ball mill for the duration of the milling. Although there was some variation of the
15 concentration of some of the additives, no attempt was made to optimise their concentrations or their reducing properties. One control experiment was carried out using ilmenite alone (that is, with no additive to the charge of the ball mill).

20 Particular additives used in the experiments were as follows:

1. DDAA (didodecyl dimethyl ammonium acetate);
2. DDAB (didodecyl dimethyl ammonium bromide);
3. DHDA (dihexadecyl dimethyl ammonium acetate);
- 25 4. DDAOH (didodecyl dimethyl ammonium hydroxide);
5. SDDS (sodium didodecyl sulphate);
6. Dodecane; and
7. Amorphous boron.

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During the milling - which lasted for up to 300 hours - the charge of the ball mill was held at room temperature (about 25°C). For experiments using the additives 1 to 5 above, the milling was performed in aqueous solution. Considering
5 the point of zero charge of the ilmenite particle, it was necessary to adjust the pH of the aqueous solution of the additives DDAA, DDAB and DHDA so that it had a value of 10, which corresponds to negatively charged ilmenite particles, in order to get adsorption of the cationic
10 species. For the experiments with the additive SDDS, the pH was adjusted to a value of 5, which corresponds to positively charged ilmenite particles, in order to get adsorption of the anionic surfactant SDDS. Potassium hydroxide and potassium chloride were used for pH
15 adjustment. No adjustment of the pH of the aqueous solution was necessary for experiments with the additive DDAOH.

The nanostructural ilmenite products obtained by milling the ilmenite with the additives (i) DDAOH, (ii) SDDS and
20 (iii) amorphous boron, were leached with 4M hydrochloric acid at temperatures ranging from 80°C to 100°C. The Rutherford backscattering spectroscopy spectra of the leached materials showed

- 25 (a) that less than 5 atomic per cent of the iron in the sample milled with DDAOH remained after leaching; and
(b) there had been a significant reduction of the iron content of the ilmenite samples that had been milled with SDDS and with amorphous boron.

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The x-ray diffraction pattern of the material milled with DDAOH and then leached with hydrochloric acid showed only peaks corresponding to rutile.

Thus the experiments showed that prolonged milling of
5 ilmenite with an appropriate additive produces a nanostructural powder that is amenable to leaching with hot hydrochloric acid to remove the iron component of the ilmenite and leave rutile (TiO_2).

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CLAIMS

1. A method of treatment of a titaniferous ore to facilitate the removal of iron from the ore to produce rutile, the method comprising high energy milling of the ore in particulate form in the presence of a suitable additive for a period sufficient to form a nanostructural titaniferous product.
2. A method as defined in claim 1, in which said additive is a reducing agent.
3. A method as defined in claim 2, in which said reducing agent is amorphous boron.
4. A method as defined in claim 1, in which said additive is a long chained hydrocarbon.
5. A method as defined in claim 4, in which said hydrocarbon is dodecane.
6. A method as defined in claim 1, in which said additive is a surfactant.
7. A method as defined in claim 6, in which said surfactant is a surfactant selected from the group consisting of:
 - (a) dihexadecyl dimethyl ammonium acetate;
 - (b) didodecyl dimethyl ammonium bromide;
 - (c) didodecyl dimethyl ammonium acetate;
 - (d) didodecyl dimethyl ammonium hydroxide; and
 - (e) sodium didodecyl sulphate.

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8. A method as defined in claim 6 or claim 7, in which said surfactant is in aqueous solution and the pH of the aqueous solution is adjusted to ensure adsorption of the surfactant by the titaniferous ore.
9. A method as defined in any preceding claim, in which the high energy milling is effected at a temperature of about 25°C.
10. A method as defined in any preceding claim, in which the high energy milling is effected for a period of about 300 hours.
11. A method as defined in any preceding claim in which the high energy milling is effected in a ball mill of the type described and claimed in the specification of International patent application No PCT/AU90/00471.
12. A method as defined in any preceding claim, in which the titaniferous ore is ilmenite.
13. A method as defined in any preceding claim, including the additional step of leaching the nanostructural titaniferous product of the milling to remove at least a major proportion of the iron therein.
14. A method as defined in claim 13, in which said leaching is effected using hydrochloric acid.
15. A method as defined in claim 14, in which said leaching is effected using 4M hydrochloric acid at a temperature in the range of from 80°C to 100°C.

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16. A method of treatment of a titaniferous ore as defined in claim 1, substantially as hereinbefore described.

INTERNATIONAL SEARCH REPORT**A. CLASSIFICATION OF SUBJECT MATTER**Int. Cl.⁶ C22B 1/00, 34/12, 3/04, 3/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC C22B 1/00, 34/12

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base, and where practicable, search terms used)

DERWENT : mill: or comminut: and titan: or ilmenite

JAPIO : mill: or comminut: and titan: or ilmenite

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	FR,A, 2351706 (THE DOW CHEMICAL COMPANY) 16 December 1977 (16.12.77) claims	1
A	US,A, 4256266 (MAGALHAES, Gustavo) 17 March 1981 (17.03.81) claims	1
A	US,A, 4197276 (TOLLEY, W K, et al.) 8 April 1980 (08.04.80) claims	1
A	US,A, 4175952 (TOLLEY, William K) 27 November 1979 (27.11.79) claims	1

Further documents are listed
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Date of the actual completion of the international search
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate of the relevant passages	Relevant to Claim No.
A	US,A, 4175110 (TOLLEY, William K) 20 November 1979 (20.11.79) claims	1
A	JOURNAL OF MINERALS, METALS AND MATERIAL SOCIETY, April 1994, Thomas S Mackey, "Upgrading Ilmenite into a High-Grade Synthetic Rutile", Pages 59-64 whole document	1-16

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
FR	2351706	AR	217252	AU	25267/77	BR	7703212
		CA	1103375	JP	53007587	JP	60036818
		SE	7705932	US	4126777	ZA	7702965
		US	4162044	US	4136830		
US	4256266	AU	43828/79	BR	7800585	CA	1118213
		JP	54148114				
US	4197276	NIL					
US	4175952	NIL					
US	4175110	NIL					
END OF ANNEX							